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BES 05/01/03

SUBSTITUTE SPECIFICATION

10/031,081

Sub Spec (NE)
3-11-03
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METHOD OF DETERMINING STRUCTURE OF SOFT MATERIAL

Technical Field

The present invention relates to a method of determining structures of low-density materials referred to as soft materials. The term "soft material" as used herein signifies a material whose structure is disordered on an atomic scale but ordered on a meso-scale (from 20 to 500 angstroms). In particular, the invention is concerned with a method of determining three-dimensional structures of soft materials by use of high-resolution transmission electron microscopy images.

Background of the Invention

In a traditional structure determination of a material, a sample of the material is extensively irradiated with beams, such as X rays, electron beams or neutron beams, and diffraction patterns (diffraction intensity curves) obtained from the irradiated volume are measured. By such a measurement, the average structure of a sample material in its entirety can be presumed. More specifically, the spatial distribution of scatterers, such as electrons, in unit cells as the smallest structural units is determined on the precondition that atoms are spaced in a completely periodic configuration, and an approximate solution thereto, or the coordinates describing the position of each atom, is determined on the assumption that each atom has a spherically symmetric electron distribution. In this case, the intensity of each diffraction point is generally measured on an individual basis by the use of a single crystal. From these intensities, the amplitudes of the structure factors are determined, and further the phases of the structure factors are estimated using some method.

By inversely Fourier transforming these structure factors, a structure of the sample material can be determined.

In general, the distribution $\rho(x,y,z)$ of a scatterer (atom) concerned with diffraction can be expanded to the following Fourier series when the crystal structure factor is represented as $F(h,k,l)$, the phase factor as $\phi(h,k,l)$ and the scatterer volume as V:

$$\rho(x,y,z)=(1/V)\Sigma(h)\Sigma(k)\Sigma(l)F(h,k,l)\exp\{-2\pi(hx+ky+lz)\} \quad \cdots(1)$$

$$F(h,k,l)=ABS\{F(h,k,l)\}\exp\{i\phi(h,k,l)\} \quad \cdots(2)$$

wherein h, k and l are indices of diffraction planes.

Accordingly, the structure $\rho(x,y,z)$ can be uniquely determined from inverse Fourier transform so long as the crystal structure factor $F(h,k,l)$, namely the amplitude $ABS\{F(h,k,l)$ and the phase $\phi(h,k,l)$, is found with respect to a number of hkl reflections.

However, the diffraction means generally adopted for structure determination (such as X-ray diffraction, electron diffraction or neutron-beam diffraction) enables nothing but measurements of diffraction intensities of hkl reflections, or the absolute values of crystal structure factors $ABS\{F(h,k,l)\}$. Unique determination of the phases $\phi(h,k,l)$ cannot be made thereby. Thus, the traditional diffraction means have a drawback in that estimations of the phases of the crystal structure factors require a premise that diffraction intensity measurements have already been made on a great number of diffraction indices.

Further, the traditional diffraction techniques as mentioned above are developed on a basis of periodicity of bonds at an atomic level, so that it is impossible for these techniques to clear up structures of soft materials. This is because, in the diffraction from a soft material structure, several reflection

lines are observed in the low scattering-angle region, while in the high scattering-angle region nothing but diffuse scattering is observed. As a result, it is impossible to obtain diffraction intensities for many reflections. For instance, the powder X-ray diffraction pattern of a mesoporous silica SBA-1, is shown in Fig. 4. From this pattern, it is impossible to determine not only a space group but also a crystal system (structural unit cell parameters $a,b,c,\alpha,\beta,\gamma$).

Summary of the Invention

The term "soft material" as used herein means a material whose structure is disordered on an atomic scale but in a good order on a meso-scale (from 20 to 500 angstroms).

As a result of our intensive studies to determine structures of soft materials, it has been found that by taking advantage of the low density of a soft material and the small dynamic scattering effect of electrons transmitted by a soft material, it becomes possible to uniquely determine the three-dimensional structure of a soft material from high-resolution transmission electron microscopy images, although univocal determination thereof was impossible by the use of traditional X-ray or electron diffraction. By this finding, we have achieved the present invention.

Therefore, an object of the invention is to provide a method of easily determining three-dimensional structures of soft materials without making assumptions, although it was hitherto difficult to determine them.

The aforesaid object of the invention is attained with a method of determining a soft material structure, comprising the steps of taking transmission electron microscopy images of soft materials with crystallographically different directions of

incident electrons, Fourier transforming each of the images photographed, evaluating therefrom amplitudes and phases of three-dimensional crystal structure factors, and further performing inverse Fourier transforms by use of the values evaluated, thereby determining a structure of the soft material.

Brief Description of the Drawings

Fig. 1 is a photograph of the high-resolution transmission electron microscopy image taken from a thin film sample of the mesoporous silica SBA-1 with electron beams in the direction [100]. Fig. 2 shows a three-dimensional structure of the mesoporous silica SBA-1 determined by the present method. Fig. 3 shows a three-dimensional structure of the mesoporous silica SBA-16. Fig. 4 shows a powder X-ray pattern (CuKα) of the mesoporous silica SBA-1 in the low scattering-angle region (2θ: 0° to 10°). The characters A and B each in Fig. 2 denote different cavities.

Detailed Description of the Invention

The soft materials whose structure is determined according to the invention, which signify materials whose structures are disordered on an atomic scale but ordered on a meso-scale (from 20 to 500 angstroms), generally include light elements, porous materials, combinations of light elements, combinations of porous materials and combinations of light elements and porous materials. More specifically, mesoporous materials, surfactants, (copolymerized) macromolecules, biological membranes and liquid crystals are included in the soft materials to which the present invention is applicable.

A transmission electron microscopy image, as is evident from its principle, is a projection of the scatterer atom distribution $\rho(x,y,z)$ viewed from the direction of incident electron beams. In

the case of Z-axis incidence, for instance, the transmission electron microscopy image is observed exactly as information concerning the x and y coordinates of the atom distribution integrated with respect to z of $\rho(x,y,z)$. In other words, a group of data for the equation $F(h,k,0) = ABS\{F(h,k,0)\}\exp\{i\phi(h,k,0)\}$ are determined uniquely on a series of reciprocal lattice points expressed as h,k,l (l=0) by the foregoing equation (1). In analogy with the above case, transmission electron microscopy images are observed respectively from a plurality of directions independent of the above, and subjected to Fourier transform processing to evaluate $F(h,k,l) = ABS\{F(h,k,l)\}\exp\{i\phi(h,k,l)\}$ with respect to reciprocal lattice points in the three-dimensional reciprocal space within the limits of resolutions of the images, and then inversely Fourier transformed. As a result, a three-dimensional structure is determined uniquely.

When the foregoing method is carried out, the mean free path of electrons inside a material is generally short because of strong interaction between the electrons and the material, and the electrons are scattered multiply during the propagation through the material sample to produce a dynamic scattering effect. Therefore, the structural analysis by such a method has so far been thought to be difficult. However, as the scattering power of a soft material is weak, the dynamic scattering effect as mentioned above becomes negligible when the thickness of a soft material sample is reduced to 50 nm or below. The preparation of such a thin sample can be performed according to known methods. The thinner the sample thickness, the better result is obtained.

In order to determine the three-dimensional structure of a soft material with satisfactorily high accuracy, it is appropriate

that a high-resolution transmission microscope be used as the transmission electron microscope in the invention, and it is desirable that at least three different crystallographically significant directions be selected as the incident directions of electrons and transmission electron microscopy images be formed under incidence of electron beams from these directions respectively. The expression "crystallographically significant incident directions of electrons" as used herein means incident-axis directions having high linear independence from one another. For instance, those incident directions are [100], [110], [111] and [211] in the case of cubic crystals. Needless to say, when transmission electron microscopy images are photographed in more directions of incident electrons and the information derived therefrom is brought into full play, higher accuracy can be attained in determination of a three-dimensional structure.

In order to perform Fourier transforms of transmission electron microscopy images in the invention, it is required that those images be formed directly on a CCD camera or photographed and then converted into electronic form by means of an image reader. From these data in electronic form, Fourier transform patterns of high-resolution images are obtained in accordance with the usual method. Then, the phases of diffracted waves are read on the assumption of weak topological object approximation. With respect to the diffracted waves in the region of high spatial frequencies, it is desirable that the influence of aberration in an objective lens be reduced through estimation of the amount of defocus by the use of a Wiener filter.

In the next place, only peaks on the reciprocal lattice points are selected, and the integral intensity of each peak, from

which background is already subtracted in accordance with the method of least squares, is measured. In the case of Fourier diffraction patterns, the phases are calculated simultaneously with the intensity measurement.

When lattice constants are undecided, they are calculated from at least two diffraction patterns obtained in the same field of view and the tilt angle of a sample stage used in each measurement. Therefrom, several sets of potential lattice constants are derived since the stage angles of now-available electron microscopes are poor in accuracy. When the lattice constants are known, index assignment is carried out for each of the diffraction patterns.

In order to perform structural analysis based on these data, the diffraction data in a TEXT file or a program memory are combined first, and then normalized on the basis of common reflection data. Further, the averaging is carried out by symmetry operation of point groups. At this point, a space group is assumed, and the combined data obtained is stored as a TEXT file.

Fourier diffraction patterns of low spatial resolution (0.3 mm or above) are data of diffraction peaks with phases, while Fourier diffraction patterns of high spatial resolution (0.1 mm or below) are data of diffraction peaks without phases.

Accordingly, each set of these data is read from the TEXT file or the program memory, and phase extension is made by conferring phases on the latter on the basis of the phases of the former.

Then, the diffraction data with phases are read from the TEXT file or the program memory, three-dimensional fast Fourier transform (3D-FFT) thereof is performed to obtain a three-dimensional potential distribution, and peak positions in

this distribution are analyzed to assign atom positions.

The invention will now be illustrated in greater detail by reference to the following examples, but these examples should not be construed as limiting the scope of the invention in any way.

Example 1

Fig. 1 is a high-resolution transmission electron microscopy image obtained by taking a thin film sample of mesoporous silica (SBA-1: Science, 279 (1998) 548-552) under irradiation with electron beams in the direction [100]. This figure shows that the sample has sufficient order on a meso-scale. Particularly in the figure, it is noted that the low-contrast image area corresponding to the periphery of the sample (having a thickness of 50 nm or below) is a region wherein dynamic scattering effect is negligible. The light-and-shade distribution of the image corresponding to the periphery part (50 nm or below in thickness) of the sample was measured with a CCD camera, and the electronic data thus obtained on the light-and-shade distribution were Fourier transformed to evaluate amplitudes and phases of the crystal structure factors. Then, a two-dimensional Fourier diffraction pattern was determined as the distribution of the squared amplitudes. Similarly to the above, transmission electron microscopy images were photographed under irradiation with electron beams incident from the directions [110], [111] and [112] respectively, and therefrom two-dimensional Fourier diffraction patterns were determined.

By the use of all of these diffraction patterns a distribution of diffraction intensities on the three-dimensional reciprocal lattice points was made. From the result obtained, it was determined that the sample has a space group of pm-3n. Further, the origin point of space coordinates was sought on the basis of

the space group determined, and structure factors F(h,k,l) of the three-dimensional reciprocal lattice space were obtained as the phase information and the amplitude information on crystal structure factors. By inversely Fourier transforming those structure factors, the scatterer distribution corresponding to the equation (1) was evaluated, and it was determined that SBA-1 has a structure shown in Fig. 2. More specifically, the structure determined is a structure with voids A and B having different sizes that are arranged in amorphous silica in a V3Si configuration (A3B). Additionally, the lattice constant "a" was 73 angstrom.

Example 2

Three-dimensional structures of mesoporous silicas SBA-6 and SBA-16 synthesized under conditions different from that of the mesoporous silica SBA-1, the structures of which had not been elucidated, were each determined using the same method as in Example 1. As a result, it was found that the mesoporous silicas SBA-6 and SBA-1 were identical in structure but different in lattice constant (a=146 angstrom in the case of SBA-6) and sizes of voids A and B. On the other hand, as shown in Fig. 3, the three-dimensional structure of SBA-16 was found to be different from those of SBA-1 and SBA-6, having voids which are about 95 angstrom in size and arranged in the form of body-centered cubic lattice and a lattice constant of 133 angstrom.